Original Article

Removal of Cd (II) in Water Samples Using Modified Magnetic Iron Oxide Nanoparticle

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ABSTRACT

Background: Heavy metals, even at low concentrations, are harmful to human health and environment. Cadmium as a heavy metal is highly toxic and can cause serious threat to living organisms. This research was designed to evaluate the adsorption potential of modified magnetic iron nanoparticles by 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol ligand for the removal of cadmium ions from water solutions.

Methods: This study was conducted in Ilam Branch, Islamic Azad University, Iran, in 2014. Modified magnetic iron nanoparticle was used as adsorbent for the removal of cadmium from aqueous solution. In batch extraction, the effects of parameters like pH of sample solution (3.0-11.0), initial metal concentrations (50-300) mgL^{-1}), contact time (1.0-10 min) and adsorbent dose (10.0-60.0 mg) were studied on the adsorption process. Modified magnetite nanoparticle was presented as the adsorbent for the removal of cadmium ions from aqueous samples and later was confirmed by flame atomic absorption spectrometry.

Results: The adsorption of cadmium ions on modified magnetite nanoparticles strongly depends on pH. The experimental isothermal data were analyzed using the Langmuir and Freundlich equations. The removal process followed the Langmuir isotherm. Maximum adsorption capacity for the adsorption of cadmium ions by the sorbent was 24.09 mgg^{-1}.

Conclusion: The method was successfully applied to adsorption of cadmium in water samples with satisfactory results. Other advantages include high capacity, good stability and fast adsorption kinetics. High pre-concentration factor was obtained easily by this method (120) and low analysis cost.

Keywords: Cadmium Ions, Flame Spectrometry, Magnetic Nanoparticle, Removal.

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INTRODUCTION

Cadmium is one of the most toxic elements and accumulates in humans mainly in the kidneys and liver. Prolonged intake of cadmium alters calcium regulation in biological systems, which induces cell injury and death. In spite of toxic and dangerous to humans and the environment is widely renowned cadmium plating, nickel-cadmium batteries, coatings, and plastics are used as stabilizers [3]. “The FAO/WHO Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of cadmium from all sources (water, food and air) of 1.0–1.2µg/kg body mass“ [4]. The maximum acceptable level of cadmium in con

The direct determination of extremely low concentrations of the required trace metals by modern spectroscopic methods is still not easy due to insufficient sensitivity of the techniques and matrix interferences [4]. Determination of trace amounts of metal ions in environmental samples requires a pre-concentration before detection by atomic absorption spectrometry [5, 6]. A variety of procedures for pre-concentration of metals, such as liquid–liquid extraction (LLE), co-precipitation, and cloud point extraction (CPE), solid phase extraction (SPE) and removal (adsorption) have been developed [7-14]. Among the presented methods, removal method is simple and quick way, therefore has been usually used [15]. Nowadays, investigation

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for finding new materials as adsorbent is an important issue to pre-concentrate transition metals traces levels. 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) ligand can be used as selective adsorbent for heavy metals and dyes [16, 17].

The aim of this study was to combine magnetic iron nanoparticle (MINPs) with 5-Br-PADAP ligand based batch extraction method for pre-concentration and adsorption of trace amounts of cadmium from water samples.

MATERIALS AND METHODS

Reagents and Materials

All solutions were prepared in deionized water using analytical grade reagents (Merck, Darmstadt, Germany). The laboratory glassware was kept in a 1.4 mol L HNO_3 solution for the night. The glassware was washed with deionized water and dried before use. The stock solutions of cadmium ions were prepared daily from Cd (II) standard solution 1000.0 mg L (Merck) by serial dilution with deionized water.

(5-Br-PADAP) ligand was purchased from (Merck, Darmstadt, Germany). Figure 1 shows the structure of (5-Br-PADAP).

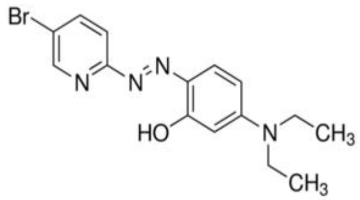

Figure 1. (5-Br-PADAP).

A solution of 10% (w/v) NaCl (Merck) was prepared by dissolving 10 g of NaCl in 100 mL of deionized water.

Batch Adsorption Experiments

The extraction method was carried out in batch process. All standards and samples were prepared according to the following procedure for analysis. Twenty-five mL of each sample were placed in a beaker. To each beaker, 2 mL of 0.1 mol L^{-1} phosphate buffer (pH 6.0), 1 mL of 10% (w/v) NaCl and 40 mg sorbent were added and was stirred for 5 min. Then, the beakers were sited on the magnet and the nanoparticles were collected. After decanting the supernatant solution, the collected MIONs were washed with 5.0 mL of 1.0 mol L HCl solution in order to elute the adsorbed analyte ions. Then, the analyte ions in the eluent were determined by flame atomic absorption spectrometry (FAAS). The uptake of metal ions in solution was calculated by differences in their initial and final concentrations. Each experiment was repeated twice and the average values were given as the results. The obtained data were employed to calculate the equilibrium metal uptake capacity according to Eq. (1):

$$qe = \frac{v(C0 - Ce)}{m}$$

Where qe (mg g) is the equilibrium amount of metal in the adsorbed phase, C_0 and Ce are the primary and equilibrium concentrations of metal ion (mg L) in the aqueous solution, and m is the sorbent dose (g) in the mixture. For studying the effect of solution pH on Cd (II) ions adsorption, experiments were conducted with different pH (varying from 3.0 to 11.0). Different amounts of adsorbent (varying from 10.0 to 60.0 mg) were used to observe the effect of adsorbent dose on Cd (II) ions adsorption. Contact times of 1, 2, 3, 5 and10 min were used to investigate the effect of contact time on adsorption. Isotherm studies were performed using different concentrations of Cd (II) (50–300 mg L) at room temperature. Removal percent of Cd (II) ions (Re %) in solution was calculated using Eq. (2):

$$Re\% = C0 - Ce/C0 \times 100$$

Where C0 and Ce (mg L^{-1}) are the initial and final concentrations of Cd (II) [18].

RESULTS

The optimum sorption properties of MINPs for cadmium ions were found using the batch technique. Quantitative recovery was obtained for cadmium using 5-Br-PADAP ligand.

PH

The adsorption of cadmium by sorbent was investigated at the pH range of 3–11. The pH of sample solutions was adjusted by 0.1 mol L NaOH or HNO_3 solutions. The results are given in Figure 2. The adsorption efficiency of the analytes was improved dramatically with increase in pH and reached maximum at pH 6.0.Therefore, pH 6.0 was used in all subsequent experiments.

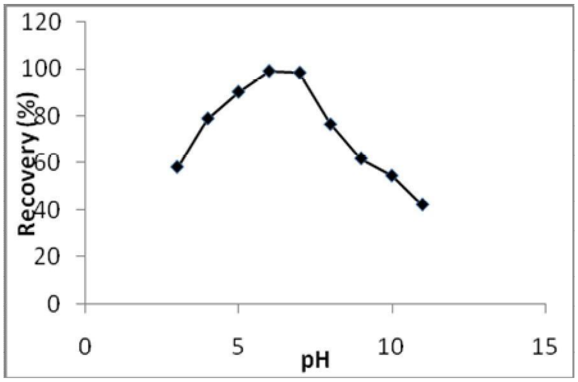

Figure 2. pH of sample solution.

Effect of Contact Time (Adsorption Kinetics)

Effect of contact time on the adsorbed amount of Cd (II) by sorbent was considered in the range of 1 to 10 min. The results are shown in Figure 3. Adsorption yield of Cd (II) by sorbent increased sharply with contact time until the equilibrium was attained. The equilibrium times for sorbent were 5 min. After it reached the equilibrium, there were no significant changes in cadmium concentration in the solution.

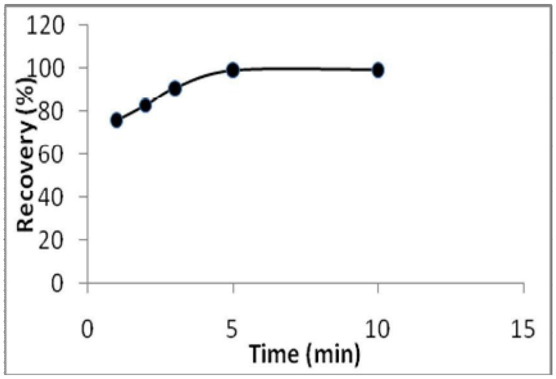

Figure 3. Effect of contact time.

Initial Concentration

The process of cadmium adsorption was considered by different initial concentrations (50, 100, 150, 200,250 and 300 mg L) while keeping adsorbent amount, pH and contact time constant. At the lowest concentration (50 mg L^{-1}), the amounts of adsorbed cadmium were 98.5% by this sorbent. The results are shown in Figure 4 that the removal efficiency decreased with increase in initial metal ion concentration.

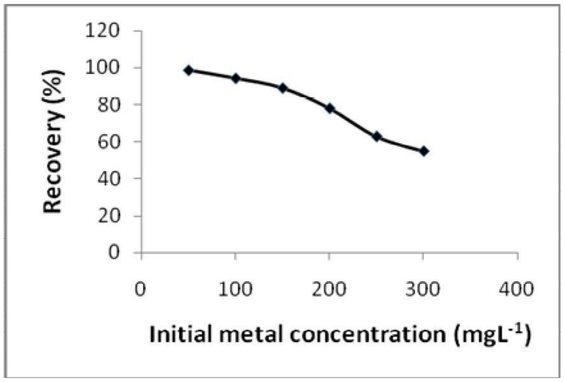

Figure 4. Effect of initial concentration.

Effect of the Adsorbent Amount

In order to study the effect of amount of the adsorbent, 10–60 mg of the sorbent was added to the sample solution. The obtained results showed that by increasing the amount of the adsorbent from 10 up to 40 mg, extraction recovery slowly increased due to the increasing of accessible sites and then remained constant (Figure 5). Therefore, 40 mg of MIONPs was used in all subsequent experiments.

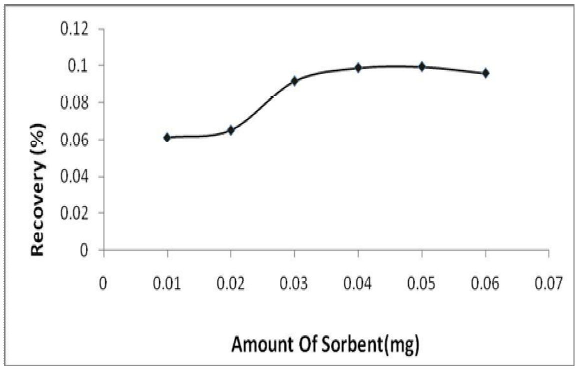

Figure 5. Amount of sorbent.

Adsorption Isotherm

The interaction between adsorbent and adsorbate are described by adsorption isotherms. Generally, the ratio between the quantity of adsorbed and that remaining in solution at a fixed temperature is at equilibrium and can be described by adsorption isotherms. In this work, both models were used to describe the relationship between the amount of cadmium ions adsorbed and its equilibrium concentration in solution at room temperature.

Langmuir Isotherm

The Langmuir equation may be written as:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}$$ (Non-linear form)

(1) $\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}$ (Linear form) (2)

Where q_e ($q_e = v(C_0 - C_e)/m$) is the amount of adsorbed cadmium per unit weight of adsorbent (mg g) and C_e is the concentration of cadmium in the solution at equilibrium (mg L^{-1}), Q_0 is the monolayer adsorption capacity (mg g^{-1}). Based on the linearized form of the adsorption isotherm derived from plots of C_e/q_e versus C_e, the constant Q_0 values were calculated from the slope of the graph (Figure 6) and b is the constant related to the free energy of adsorption ($b \propto \exp(-\Delta G/RT)$. The constants of the Langmuir isotherm are obtained by plotting C_e/q_eversus C_e. The obtained linearization shows that at equilibrium concentrations, Q_0=24.09 mgg^{-1}, b = 4.47 and coefficient (R^2) = 0.9973.

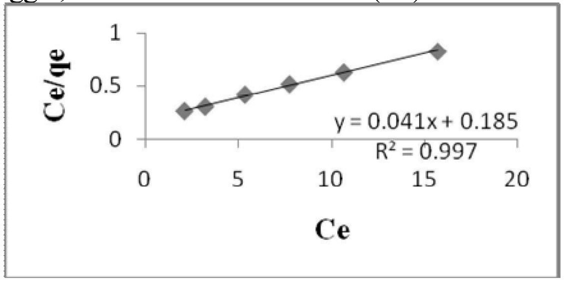

Figure 6. Langmuir isotherm.

Freundlich Isotherm

The Freundlich isotherm may be written as:

$$q_e = K_f C_e^{1/n}$$ (Non-linear form) (3)

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$ (Linear form) (4)

Where K_f is the constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and 1/n is the constant indicative of the intensity of the adsorption. The equilibrium isotherm data was fitted in Freundlich equation as illustrated in Figure 7, where the values of K_F and n are 6.26 and 2.47, respectively. The value of the coefficient of determination R^2= 0.965. Comparing between Langmuir and Freundlich results at the higher correlation coefficient (0.9973) showed that Langmuir model was more suitable than Freundlich model for adsorption equilibrium of cadmium.

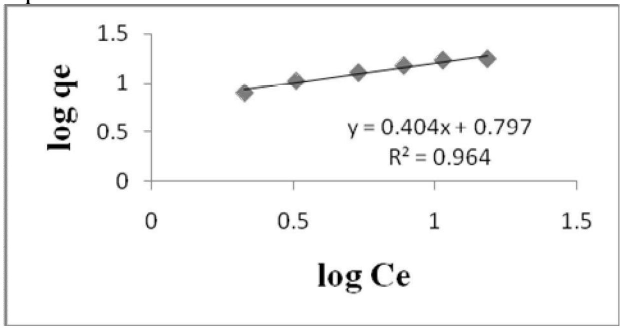

Figure 7. Freundlich isotherm.

DISCUSSION

The initial pH of solution plays a vital role in the adsorption process, particularly on the adsorption capacity by controlling the surface charge of the adsorbent and the degree ofionization of the materials in the solution. The increase in the adsorption of Cd (II) on 5-Br-PADAP with increase in the solution pH can be explained based on the surface charge of 5-Br-PADAP and the metal molecules. The results showed that the Cd (II) removal was much higher in pH=6.

At lower pH, the 5-Br-PADAP surface will be positively charged, creating electrostatic repulsion between the positively charged surface of the 5-Br-PADAP and the metals ions. The number of positively charged sites is reduced at higher pH, so raises the number of negatively charged sites, which increases the electrostatic attractions between metals ions and 5-Br-PADAP surface. The effect of solution pH on the adsorption of metals could be explained by considering competition between H^+ ions and Metal (II) ions for the active surface sites in acidic solutions. Similar phenomenon has also been shown in the adsorption of Cd (II) ion from water [19-21].

Optimizing the effect of time in adsorption systems is necessary to develop cost effective procedures. Figure 3 show the effect of contact time on the adsorption of Cd (II) ions by sorbent. Removal was rapid at the initial stages and gradually decreased with the progress of adsorption until reaching equilibrium at about 5 min. At the initial contact time, the rate of adsorption was fast due to high amounts of available adsorbent surface. The lesser efficiency of adsorption after a lapse of time could be due to two reasons. First, occupying the sites reduced the availability of active surface sites on the adsorbent. Second, the remaining vacant surface sites were difficult to be occupied due to repulsive force of the adsorbed metal ions on the solid and bulk phase. This phenomenon was also observed by other authors in removal of Cadmium from water using natural phosphate as adsorbent [22].The contact time by modified magnetic was less than the Natural phosphate as adsorbent [22].

One of the parameters that strongly affect the adsorption capacity is the adsorbent dose. As it is clear from Figure 5, the removal ratio increased rapidly with an increase in the adsorbent dose up to 40.0 mg, and afterwards the removal ratio reached almost a constant Value in 60.0 mg dose. This can be attributed to the increase in the adsorbent surface area and availability of more active adsorption sites on the MINPs-5 Br-PADAP surface with the increase for adsorbent. Therefore, 40.0 mg adsorbent was selected for subsequent works. This phenomenon was also observed by other authors who studied the efficiency of chitosan for the removal of Pb (II), Fe (II) and Cu (II) Ions from aqueous solutions and indicated that adsorption percentage increases with increasing adsorbent dose [23]. The higher correlation coefficient for Langmuir model indicated that the Langmuir model fitted the adsorption data better than the Freundlich model, which indicated the homogeneous distribution of active sites on the surface of sorbent. The results showed that the maximum adsorption capacity value for the adsorption of Cd (II) ions by the sorbent was 24.09 mg g^{-1}. Comparison of the extraction procedure with the other reports showed that the obtained sorption capacity of modified magnetic iron nanoparticles for cadmium ions is greater than those of reported in the literature [24-27].

CONCLUSION

The studied method is very suitable for the rapid extraction of cadmium ions from various samples at ppm levels with good accuracy and precision. moreover, it can be concluded from the results that modified MIONs-5-Br-PADAP are an effective sorbent for separation and pre-concentration of trace amounts of cadmium from water samples. These modified magnetic nanoparticles carrying the target metal could be easily separated from the aqueous solution simply by applying an external magnetic field with no filtration or centrifugation. In addition, the proposed method can be a guideline for the extraction of other metal ions from environmental samples.

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